# Catalytic ozonation of sulfonated aromatic compounds in the presence of activated carbon

P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira *

*Laboratório de Catálise e Materiais, Departamento de Engenharia Química, Faculdade de Engenharia,
Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

## Abstract

The ozonation of two model compounds (benzenesulfonic acid and sulfanilic acid) was carried out in the presence of activated carbon. With the aim of evaluating the role of the activated carbon surface chemistry during the ozonation, two activated carbon samples were assessed. Activated carbon promoted ozonation increased the rate of removal of the selected aromatic compounds and, most of all, enhanced the removal of organic matter. Selected experiments were carried out in the presence of a radical scavenger, which evidenced the participation of HO$^{\bullet}$ radicals in the oxidation mechanism in the degradation of benzenesulfonic acid and in the mineralization of oxidation by-products. No significant effect was observed in the degradation of sulfanilic acid. The removal of organic carbon content from solution is due to a complex mechanism involving direct ozone reactions, adsorption and free radicals mechanisms occurring both in the liquid phase and on the activated carbon surface. Regardless of its nature, activated carbon acts both as an adsorbent of the solutes and as a catalyst in the ozonation reaction, though best results are achieved with the most basic activated carbon sample.
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## 1. Introduction

Sulfonated aromatic compounds as well as aromatic amines are released into the environment in large amounts, mainly through the discharge of industrial effluents. Aromatic sulfonates are used in the production of azo dyes, drugs, detergents, etc. [1]. Production and biodegradation of dyestuffs, represent one of the main sources of these recalcitrant pollutants, especially azo dyes, which is one of the largest class of dyes applied in textile processing [2]. Generally, textile effluents are treated through conventional biological processes. The biodegradation of azo dyes may proceed in two stages. The first one involves the reductive cleavage of –N=N-moieties in anaerobic conditions, resulting in the formation of hazardous aromatic amines, such as aminobenzenesulfonic acids. The second path involves the aerobic degradation of the latter compounds. Sulfonated aromatic amines constitute a group of

aromatic compounds particularly difficult to degrade. Many of those formed during the reduction of sulfonated azo dyes are not susceptible to anaerobic or aerobic biodegradation, and conventional biological treatments fail to mineralize most of these compounds [1,2]. The organosulfonate group plays an important role in altering the solubility and dispersion properties of the molecule and increases its refractory character to biodegradation due to the thermodynamic stability of the carbon-sulfur bond [3]. Consequently, effluents from dye-houses and textile industries are often contaminated with sulfonated aromatic compounds. Chemical oxidation processes may be used as an alternative and/or as a complement to biological treatments, in order to accomplish a faster and higher mineralization of these compounds.

Ozonation and catalytic ozonation processes have been widely studied in the scope of wastewater treatments. Heterogeneous catalytic ozonation aims to enhance removal of more refractory compounds through the transformation of ozone into more reactive species and/or through adsorption and reaction of the pollutants on the surface of the catalyst. Different supported and unsupported catalysts have been tested in the ozonation of several organic compounds [4]. Among the

* Corresponding author.
  *E-mail addresses:* pfaria@fe.up.pt (P.C.C. Faria), jjmo@fe.up.pt
(J.J.M. Órfão), fpereira@fe.up.pt (M.F.R. Pereira).

studied materials, activated carbon (AC) has been found to be an attractive alternative to the treatment of wastewaters containing dyes or other organic contaminants [5–11]. Recently, the removal of naphtalenesulfonic compounds from aqueous solutions has been successfully accomplished by ozonation in the presence of activated carbon [7]. Activated carbon is believed to promote the decomposition of aqueous ozone [12–16], leading to the formation of oxygen active species both in the liquid phase and on the carbon surface, that are responsible for enhancing the mineralization of organic compounds.
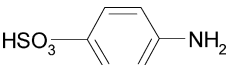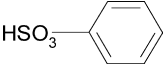
In this work, two aromatic sulfonated compounds, sulfanilic acid and benzenesulfonic acid, have been selected as model compounds. The main goal was to study the catalytic ozonation of these two aromatic acids, in order to clarify the reaction mechanism and understand the influence of the activated carbon surface chemistry on the removal of those compounds and on the mineralization of the corresponding solutions. The most significant final oxidation products detected were also followed. As pH values influence not only ozone decomposition in aqueous solution [14], but also surface properties of activated carbon [17] and dissociation of organic molecules in water, two levels of pH were studied.

## 2. Experimental

### 2.1. Materials

Sulfanilic acid (SA) and benzenesulfonic acid (BSA) were obtained from Sigma–Aldrich. Some properties of these compounds are presented in Table 1. A commercial activated carbon, Norit GAC 1240 PLUS (sample $AC_0$), was submitted to an oxidation treatment in the liquid phase with $HNO_3$ 6 M under boiling temperature during 3 h (sample $ACHNO_3$) [14]. The textural characterization of the materials was based on the $N_2$ adsorption isotherms determined at 77 K. The surface chemistry of the activated carbon samples was characterized by the determination of acidity and basicity, $pH_{pzc}$, and temperature-programmed desorption (TPD), as described elsewhere [18]. No major differences were observed regarding the textural properties of the activated carbon samples [19]. Sample $AC_0$ has a BET surface area of 909 $m^2/g$. It is a fairly basic activated carbon with a $pH_{pzc}$ of 8.5. Sample $ACHNO_3$ has a BET surface area of 827 $m^2/g$ and $pH_{pzc}$ of 3.0. A more detailed characterization of these materials is reported elsewhere [14].

Table 1
Properties of the selected aromatic compounds

| Solute | M (g/mol) | p$K_a$ |
|---|---|---|
| Sulfanilic acid (SA) | 173.2 | 2.92[*] |
| Benzenesulfonic acid (BSA) | 158.2 | −2.36 |

[*] p$K_a$ corresponding to the group $NH_3^+$.

### 2.2. Ozonation experiments

The removal of SA and BSA from aqueous solutions at different pH values was investigated in a slurry lab-scale reactor equipped with agitation and recirculation jacket. For comparative purposes, both adsorption on activated carbon and ozonation experiments in the absence of activated carbon were performed in the same system, under identical experimental conditions. The two activated carbons mentioned before were assessed. The reactions were carried out at the natural pH of the acids solutions, which was 3.0 for BSA and 3.3 for SA, and at pH 7. In the latter case, a phosphate buffer solution (0.01 M) was used to maintain the solution pH. In each experiment the reactor was filled with 700 mL of acid solution at a concentration of 1 mM and at the desired pH. In the adsorption and catalytic experiments, 350 mg of activated carbon (particle size: 100–300 μm) were introduced in the reactor. In the experiments carried out in the presence of *tert*-butanol, a concentration of 10 mM of this radical scavenger was used. Other experimental conditions and procedures are reported elsewhere [20].

The concentrations of both aromatic acids and detected intermediates (oxalic acid, maleic acid, oxamic acid and nitrates) were followed by HPLC using a Hitachi Elite Lachrom HPLC equipped with a diode array detector. The stationary phase was a YMC Hydrosphere C18 column (250 mm × 4.6 mm) working at room temperature. Sulfanilic acid and respective degradation compounds were analysed under isocratic elution with a mixture of water, acetonitrile and *o*-phosphoric acid at pH 2.0. In the case of benzenesulfonic acid, HPLC measurements were done under isocratic elution with a mixture of water, $NaH_2PO_4$ and *o*-phosphoric acid at pH 2.8. Ammonium ion concentration was measured with a WTW NH500 ammonia-selective electrode. The degree of mineralization was followed by TOC analysis in a Shimadzu TOC-5000A Analyzer.

## 3. Results and discussion

Kinetic experiments of ozonation in the presence of the activated carbons have been carried out for both compounds at two pH levels. For comparative purposes, experimental data on adsorption and single ozonation are also presented. A detailed study on the adsorption of the selected compounds on the same activated carbon samples has been presented elsewhere [21]. In the following sections the results obtained for BSA and SA degradation are presented and discussed separately.

### 3.1. Degradation of benzenesulfonic acid

Benzenesulfonic acid ozonation was first carried out at its natural pH, which is 3.0. Benzenesulfonic acid is a strong acid (p$K_a$ = −2.36); therefore, it is in its corresponding deprotonated form both at pH 3 and 7. Under the selected experimental conditions, the single ozonation of BSA led to a complete conversion in approximately 80 min at pH 3.0 (Fig. 1a). The simultaneous use of ozone and activated carbon enhanced the
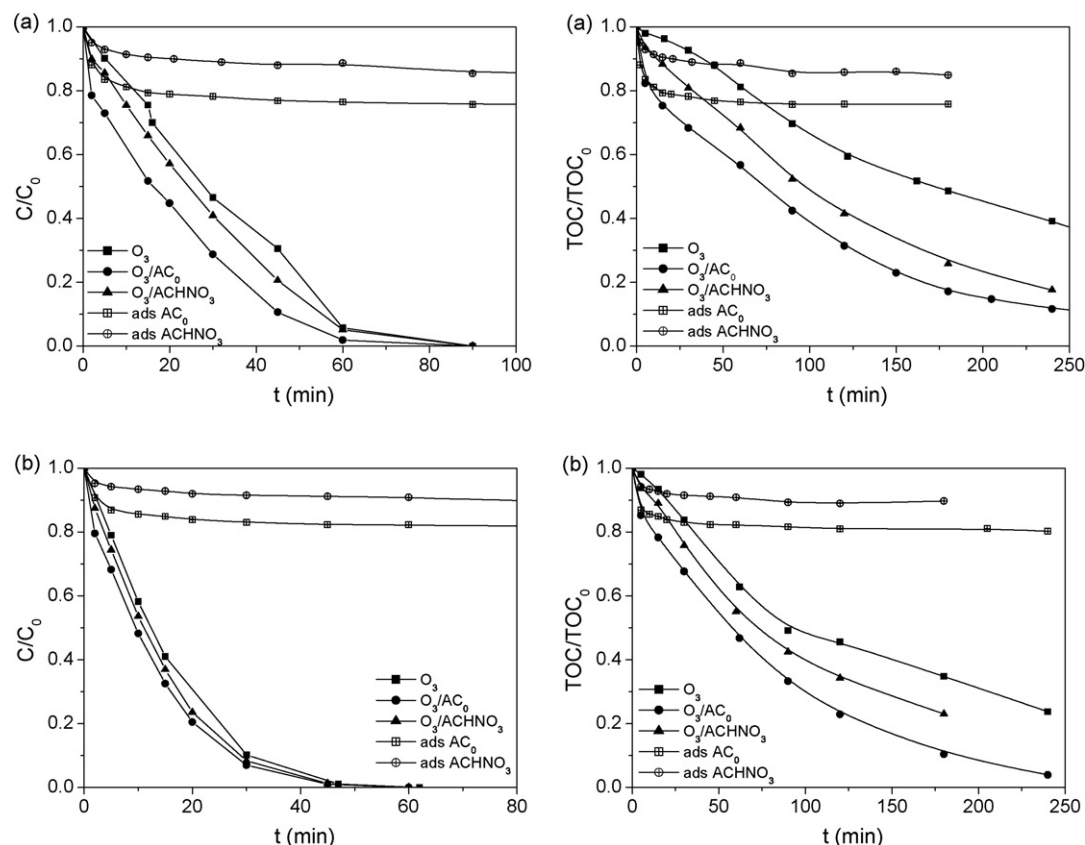
Fig. 1. Dimensionless BSA and TOC concentrations during adsorption, single ozonation and ozonation of BSA in the presence of AC at pH 3 (a) and pH 7 (b) ($C_0 = 1$ mM, AC = 0.5 g/L).

removal of BSA from solution, and better results were achieved with the fairly basic activated carbon (sample $AC_0$).

The same trend was observed in terms of TOC removal, reinforcing the importance of the activated carbon in the removal/mineralization of both BSA and oxidation by-products. During the first 10 min of reaction, the ozonation does not lead to any significant TOC removal. In fact, TOC removal observed in this period in the catalytic reaction might be due to adsorption contribution. However, after approximately 15 min, the adsorption apparently tends to a plateau. Even though it is not yet in equilibrium, the decrease in BSA concentration is very small. For longer reaction times there is an evident synergistic effect in the simultaneous use of ozone and activated carbon. The mineralization rate is significantly improved by the presence of both activated carbon samples, which is not explained by the sum of single ozonation and adsorption contribution. After 180 min of reaction the TOC removal achieved with samples $AC_0$ and $ACHNO_3$ was 83% and 74% respectively, against 51% achieved with single ozonation.

The ozonation of BSA originates numerous intermediary products which identification was not always possible to accomplish. In this particular case we were interested in identifying final oxidation products highly refractory to ozonation in order to evaluate the role of the activated carbon in their mineralization. In the case of BSA, oxalic acid was identified as one of the main reaction intermediates that

persisted in solution and was monitored during the reaction period. The results obtained are depicted in Fig. 2. In addition, the mineralization of aromatic sulfonates results in the release of the sulfur moiety. Accordingly, the ozonation of BSA results in the formation of $SO_4^{2-}$ (data not shown).

The low reaction rate constants reported in the literature for the ozonation of oxalic acid and their corresponding anions ($k < 0.04$ M$^{-1}$ s$^{-1}$ at pH > 5) explain why such compounds always accumulate as final products when organic aqueous
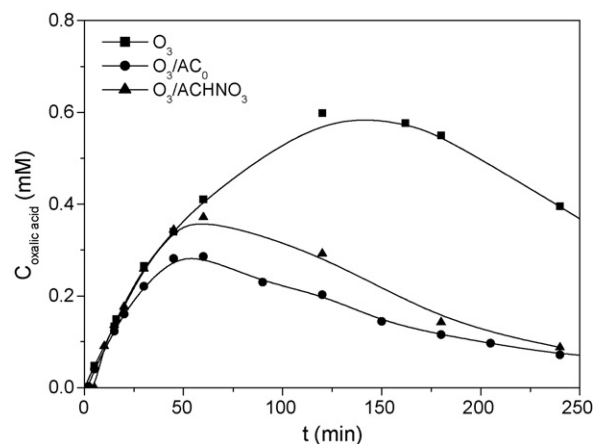


Fig. 2. Evolution of oxalic acid concentration during catalytic and non-catalytic ozonation of BSA at pH 3 ($C_0 = 1$ mM, AC = 0.5 g/L).

solutes are ozonized in water [22]. The compounds of low reactivity towards ozone may be oxidized by secondary oxidants such as hydroxyl radicals produced during the decomposition of ozone in aqueous solution. In fact, oxalic acid reacts with HO$^\bullet$ radicals with a rate constant of approximately $10^6\,M^{-1}\,s^{-1}$ [23]. Oxalic acid can also be oxidized through heterogeneous catalytic reactions in the presence of activated carbon or other catalysts [20,24,25].

In the experiments carried out, it was observed that the amount of oxalic acid accumulated in solution was always lower when ozonation was carried out in the presence of AC, which clearly indicates an enhancement in the mineralization of this compound. Therefore, the role of activated carbon in the ozonation of organic compounds becomes crucial in the degradation of oxidation by-products. Sample $AC_0$ led to lower concentrations of oxalic acid than sample $ACHNO_3$, which is in agreement with the results reported by the authors for the ozonation of oxalic acid catalyzed by activated carbon [20].

The rate of removal of BSA by single ozonation was significantly higher at pH 7 than at pH 3 and complete disappearance of BSA was achieved in ca. 45 min (Fig. 1b). This behaviour is in accordance with what was expected, as the increase of solution pH leads to an increase in the ozone self-decomposition originating HO$^\bullet$ among other reactive oxygen-containing radical species. Hydroxyl radicals are responsible for the oxidation of a vast number of organic compounds. In this case, the increase in the rate of degradation by single ozonation is attributed to a higher concentration of HO$^\bullet$ in solution at pH 7, comparatively to pH 3 where direct ozone reactions predominate.

At pH 7 the simultaneous use of ozone and activated carbon resulted only in a slight increase in the removal rate of BSA. A more distinct effect was observed in terms of TOC removal, especially for sample $AC_0$ that significantly enhanced the extent of mineralization. After 180 min of reaction the TOC removal achieved with samples $AC_0$ and $ACHNO_3$ was 90 and 77%, respectively, against 65% attained in single ozonation. The effect of pH is more pronounced in single ozonation than in the presence of activated carbon, where this effect is lessened.
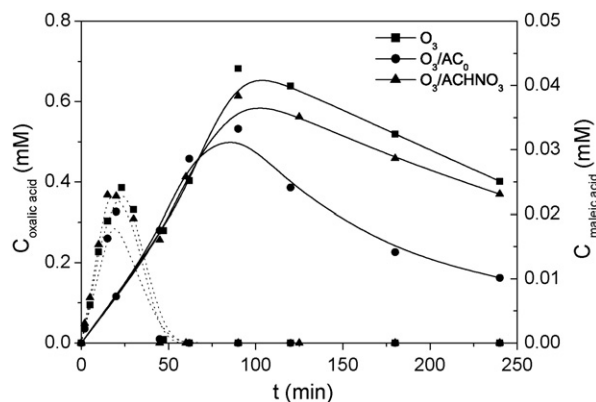


Fig. 3. Evolution of oxalic acid (solid lines) and maleic acid (dotted lines) concentrations during catalytic and non-catalytic ozonation of BSA at pH 7 ($C_0 = 1$ mM, AC = 0.5 g/L).

Among all the oxidation intermediates present in the reaction samples chromatograms, maleic acid (only trace amounts were observed at pH 3) and oxalic acid were identified and quantified along time. According to Fig. 3, maleic acid accumulated in solution during the first minutes of reaction and was easily oxidized by ozone. After ca. 45 min of reaction no maleic acid was detected.

As previously stated, oxalic acid is described in the literature as being refractory to direct ozonation. Nevertheless it is prone to be oxidized by the attack of HO$^\bullet$ radicals or by oxidation on the surface of the activated carbon. Fig. 3 shows that, in the presence of activated carbon, particularly sample $AC_0$, the concentration of oxalic acid resulting from the oxidation of BSA at pH 7 is lower than that obtained in single ozonation, which implies a faster removal of this compound from water. When comparing the results at both studied pH, it was found that oxalic acid was more efficiently removed at pH 3 than at pH 7. During single ozonation, the evolution of the concentration of oxalic acid was quite similar independently of the solution pH. In the presence of activated carbon, the concentration of oxalic acid is always lower at pH 3 than at pH 7, indicating that the conversion for this compound is higher at acidic pH. These observations are consistent with the results obtained during the
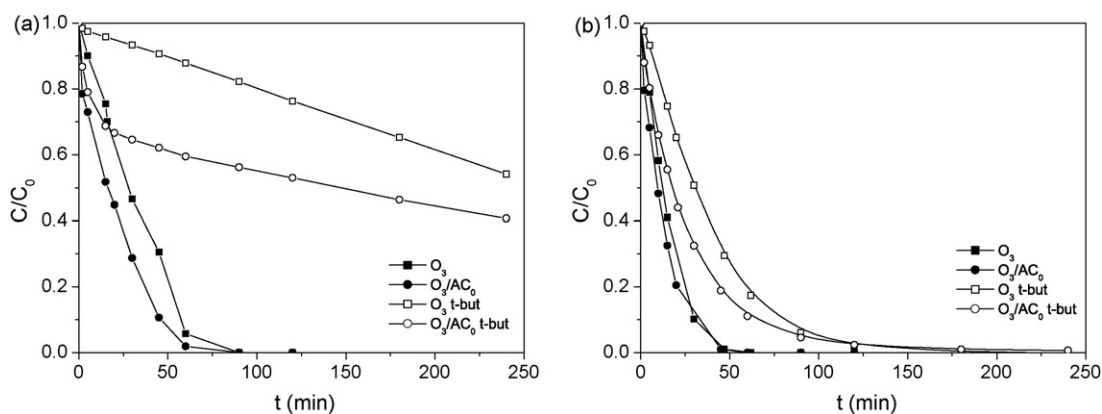


Fig. 4. Influence of *tert*-butanol on the dimensionless BSA concentration during single ozonation and ozonation in the presence of $AC_0$ at pH 3 (a) and pH 7 (b) ($C_0 = 1$ mM, AC = 0.5 g/L, $C_{t-but} = 10$ mM).

study of oxalic acid ozonation promoted by activated carbon [20].

In order to better understand the ozonation mechanism of BSA, a few experiments were carried out in the presence of a well know radical scavenger. Due to its HO$^\bullet$ radical scavenging action, *tert*-butanol was added to the solution, in order to suppress the reactions in the bulk between the BSA or the corresponding organic by-products, and the HO$^\bullet$ radicals. The results obtained at pH 3 and pH 7 are depicted in Fig. 4.

It was observed that the presence of *tert*-butanol inhibited the removal rate of BSA at both acid and neutral pH. As shown before, the ozonation of BSA is enhanced by an increase in the solution pH, which might be explained by a higher concentration of HO$^\bullet$ radicals in solution that contributes to a faster degradation of BSA. This fact, together with the negative impact of the presence of *tert*-butanol in the reaction, evidences that the complete removal of BSA is hardly accomplished only by molecular ozone attack. This provides experimental evidence that even at pH 3 the oxidation of BSA occurs via a radical mechanism involving HO$^\bullet$ radicals as main oxidizing species. The ozone attack to the aromatic ring system is highly electrophilic and also highly selective. It is known that the substituent –HSO$_3$ is a strongly deactivating group for that attack, since it decreases the electron density at the *ortho*- and *para*- positions of the ring through a resonance withdrawing effect. Hence these sites are less nucleophilic and therefore, less prone to electrophilic attack by molecular ozone.

At pH 7 the decomposition of ozone into radical species is highly accelerated due to the high concentration of HO$^-$, which acts as an initiator of ozone decomposition. Therefore, a higher concentration of HO$^\bullet$ radicals is expected when compared to pH 3. In the presence of *tert*-butanol the degradation rate of BSA by single ozonation decreases significantly due to HO$^\bullet$ scavenging. In the same way, the catalytic ozonation of BSA is also inhibited. However the results are still better in the presence of AC$_0$, which suggests that another oxidation mechanism, such as surface reactions, also co-exists.

The effect of the radical scavenger in the degradation of BSA is also evident when analyzing the concentration of oxalic acid along time (Fig. 5).

As already said, oxalic acid is formed from the oxidation of BSA and is slowly mineralized during the reaction. At pH 3 (Fig. 5a), low concentrations of oxalic acid are detected in solution, which is due to the fact that BSA degradation is highly inhibited by the presence of the radical scavenger. Nevertheless, at pH 7, when BSA is more effectively converted, higher concentrations of oxalic acid are detected along time. For single ozonation in the presence of *tert*-butanol, oxalic acid accumulates in solution at least during the first 4 h of reaction, due to its refractory character towards molecular ozone attack [20,24]. On the contrary, in the presence of AC$_0$ and *tert*-butanol, it seems that oxalic acid concentration passes through a maximum, meaning that it is being removed. Even though the presence of *tert*-butanol inhibits the oxidation of oxalic acid via HO$^\bullet$ radicals in solution, this compound is believed to be oxidized on the surface of the activated carbon through a catalytic ozonation mechanism [20]. At pH 7 also maleic acid is identified as one of the final oxidation products. As was shown in Fig. 3, after 45 min of reaction, in the absence of the radical scavenger, no maleic acid was found in solution. On the opposite, in the presence of *tert*-butanol, maleic acid is slowly formed and accumulates in solution during the first 4 h of reaction.

### 3.2. Degradation of sulfanilic acid

The catalytic ozonation of sulfanilic acid was carried out at pH 3.3 (natural solution pH) and pH 7. As shown in Fig. 6, sulfanilic acid is easily oxidized during single ozonation regardless of the solution pH. At acid pH, the addition of activated carbon to the ozonation process slightly improves its removal rate. This effect might be mostly due to the adsorption contribution than to a catalytic oxidation mechanism. At pH 7 no remarkable differences are observed between non-catalytic and catalytic ozonation. In fact, at neutral pH this compound adsorbs less on both activated carbon samples, which corroborates the above explanation. Moreover, no major differences are observed between the results obtained by single ozonation at pH 3.3 and pH 7. This leads to the conclusion that the oxidation of SA is not strongly improved by
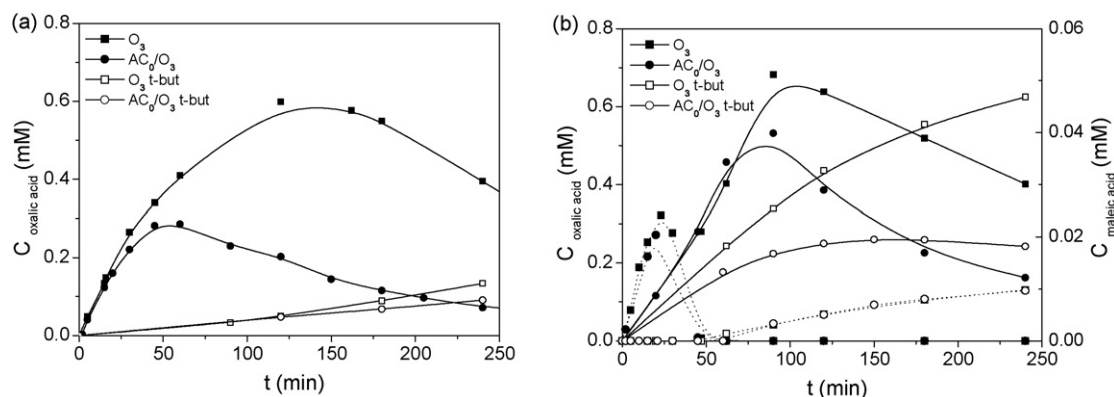


Fig. 5. Influence of *tert*-butanol ($C = 10$ mM) on the concentrations of oxalic acid (solid lines) and maleic acid (dotted lines) resultant from the single ozonation and ozonation of BSA in the presence of AC$_0$ at pH 3 (a) and pH 7 (b).
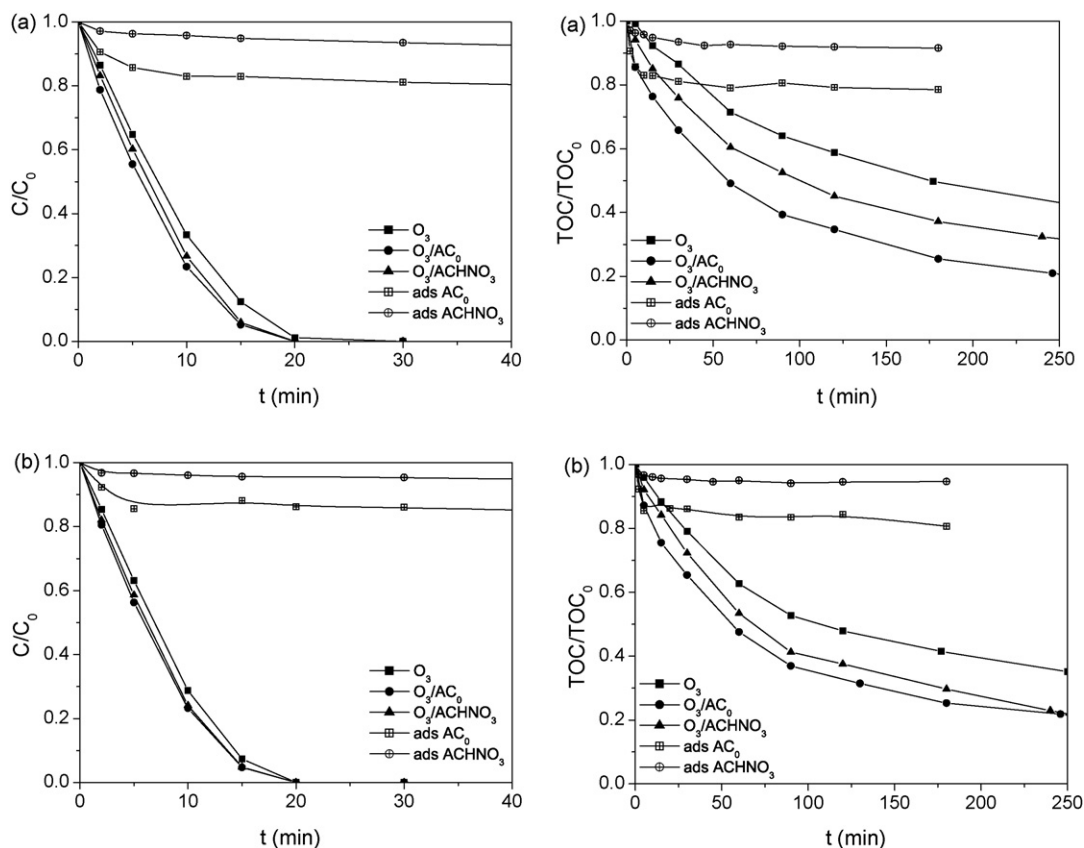
Fig. 6. Dimensionless SA and TOC concentrations during adsorption, single ozonation and ozonation of SA in the presence of AC at pH 3.3 (a) and pH 7 (b) ($C_0 = 1$ mM, AC = 0.5 g/L).

a higher rate of ozone decomposition into oxygen-containing radicals, which are more reactive species.

On the other hand, an enhanced TOC removal is observed at pH 3.3 and pH 7 when activated carbon and ozone are used simultaneously. Both the pH effect and the catalytic effect produced by the presence of activated carbon are more visible when analyzing the concentrations of final oxidation products, such as small chain carboxylic acids. These compounds are usually refractory to molecular ozone attack, but react more effectively with HO• radicals or through heterogeneous catalytic mechanisms.

Even though SA seems to be less refractory to oxidation than BSA, higher TOC removals are attained for solutions of the latter compound (cf. Figs. 1 and 6). This is related with the characteristics of the intermediates formed that are expected to be more refractory for SA. Actually, in the degradation of sulfanilic acid, oxalic acid and oxamic acid are formed and the latter is an extremely refractory carboxylic acid [20,26].

Both carboxylic acids concentrations were followed, as these two compounds accumulate in solution and are responsible for the greatest fraction of TOC in solution at the end of the reaction. The results are depicted in Fig. 7.

At pH 3.3 both acids are refractory to single ozonation but their mineralization rate is greatly enhanced in the presence of activated carbon, mainly in this case of oxalic acid. In presence of activated carbon the corresponding concentrations are always lower, which indicates a faster removal rate,

especially with sample $AC_0$. In a previous work [20], oxamic acid was found to be highly refractory to single ozonation. The ozonation catalyzed by activated carbon enhanced the mineralization of oxamic acid at low pH. However, at neutral and basic pH no significant mineralization was accomplished. As expected, during the oxidation of sulfanilic acid at pH 3.3, the presence of activated carbon enabled the decrease of oxamic acid concentration in solution. On the other hand, at pH 7 no major differences in oxamic acid concentrations are observed when comparing catalytic with non-catalytic ozonation, which is in agreement with our previous results [20].

The mineralization of SA is accompanied by the conversion of its initial nitrogen and sulfur moieties into inorganic ions. Both ammonium $NH_4^+$ and nitrate $NO_3^-$ ions were detected during the ozonation of SA. Fig. 8 depicts the evolution of the concentrations of those inorganic ions during single ozonation and ozonation in the presence of activated carbon at pH 3.3 and pH 7.

During the first 30 min of reaction there is a fast accumulation of $NH_4^+$, probably due to the quick conversion of N-containing products in the early stage of the ozonation process, and it is coincident with the disappearance of SA. For longer reaction times, the $NH_4^+$ concentration does not change, pointing out that the decomposition of refractory intermediates produced during the oxidation of SA does not lead to the release of $NH_4^+$. During the oxidation process $NO_3^-$ is formed and accumulates in solution. According to the experimental results,
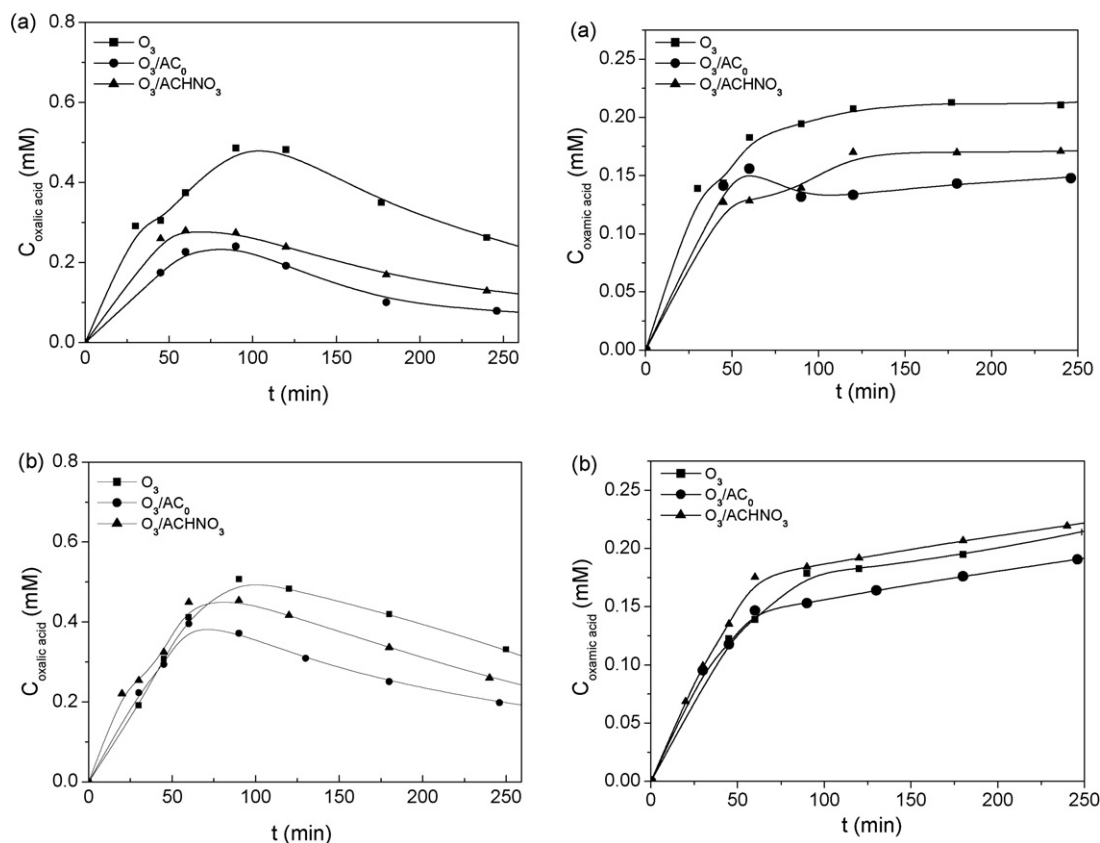
Fig. 7. Evolution of oxalic acid and oxamic acid concentrations during catalytic and non-catalytic ozonation of SA at pH 3.3 (a) and pH 7 (b) ($C_0 = 1$ mM, AC = 0.5 g/L).
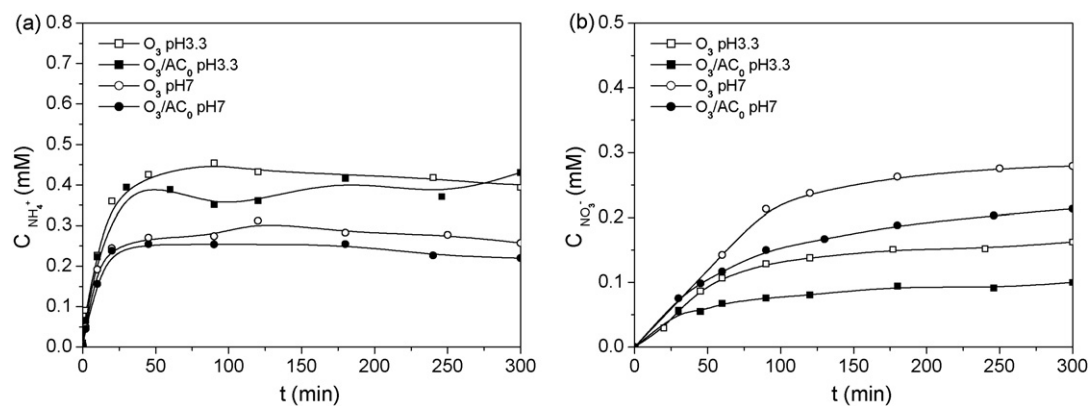


Fig. 8. Evolution of $NH_4^+$ (a) and $NO_3^-$ (b) concentrations during catalytic and non-catalytic ozonation of SA at pH 3.3 and pH 7 ($C_0 = 1$ mM, AC = 0.5 g/L).

the formation of $NH_4^+$ is favoured at acid pH and production of $NO_3^-$ at pH 7. This observation suggests different reaction mechanisms depending on the solution pH. However, the lack of knowledge of great part of the reaction intermediates makes us unable for a more detailed discussion on this matter.

Regardless of the solution pH, the concentrations of $NO_3^-$ were always lower whenever the ozonation of SA was carried out in the presence of activated carbon. This might be due, to the formation of different N-containing intermediates in the presence or absence of activated carbon and to the adsorption of some of those intermediates. Moreover, the ozonation of such

compounds in the presence of activated carbon may follow a route that does not lead to the formation of $NO_3^-$, as was reported for the catalytic ozonation of oxamic acid [20].

As previously shown (Fig. 6), the elimination of SA by single ozonation is not severely influenced by the solution pH in the range studied, i.e., similar removal rates are observed at acid and neutral pH. This might mean that the oxidation mechanism of SA is not highly dependent on the concentration of $HO^\bullet$ radicals in solution. In fact it was observed that, oppositely to what happened with BSA, the presence of a radical scavenger did no inhibit the decay of SA concentration. In fact, the
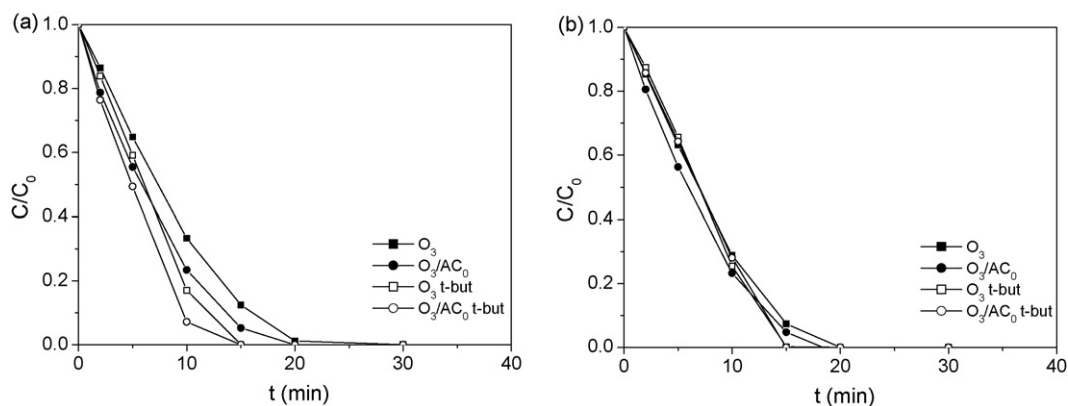
Fig. 9. Influence of *tert*-butanol on the dimensionless SA concentration during single ozonation and ozonation in the presence of $AC_0$ at pH 3.3 (a) and pH 7 (b) ($C_0$ = 1 mM, AC = 0.5 g/L, $C_{t-but}$ = 10 mM).

elimination of SA at pH natural seems to be slightly favoured by the presence of *tert*-butanol, while at pH 7 no significant differences were observed, as shown in Fig. 9. The positive effect observed at pH 3.3 might be ascribed to a stabilization of the dissolved ozone. In the presence of *tert*-butanol, $HO^\bullet$ species (which participate in the ozone decomposition chain-reaction mechanism) are consumed, slowing down the decomposition of ozone.

The experimental results suggest that sulfanilic acid molecule is more easily oxidized than the BSA molecule. The presence of the strong activating group $-NH_2$, activates the aromatic ring by increasing its electron density through a resonance donating effect. The resonance allows electron density to be positioned at the *ortho-* and *para-* positions. Hence these sites are more nucleophilic, and the system tends to react with electrophiles at these sites. Therefore, sulfanilic acid is susceptible of being attacked by molecular ozone preferentially at those sites.

Similarly to what was described for the BSA, the effect of the radical scavenger is visible when analyzing the evolution of the concentrations of both carboxylic acids followed during the ozonation of sulfanilic acid (Fig. 10).
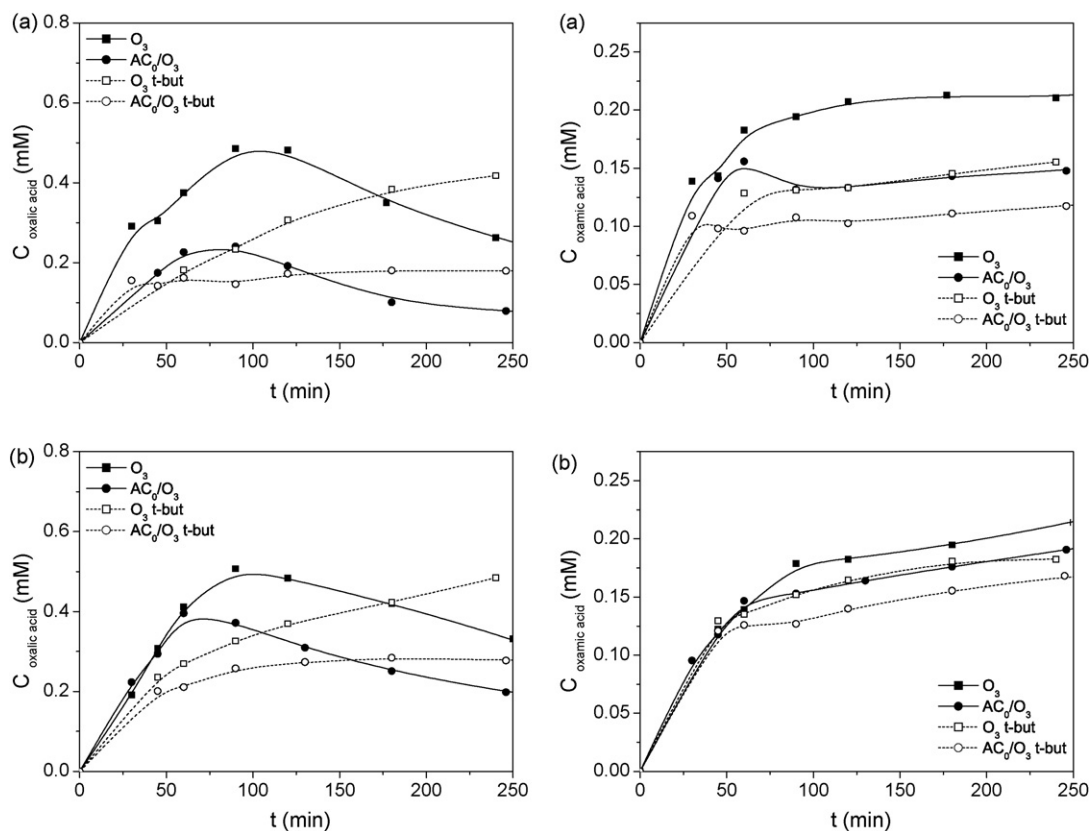


Fig. 10. Influence of *tert*-butanol ($C$ = 10 mM) on the concentrations of oxalic and oxamic acids resultant from single ozonation and ozonation of SA in the presence of $AC_0$ at pH 3.3 (a) and pH 7 (b).

During single ozonation of SA in the presence of the radical scavenger, oxalic acid accumulates in solution during the first 4 h, while in the presence of activated carbon it seems that oxalic acid is simultaneously being formed and removed, as the concentration is approximately constant after an initial accumulation period (lower at pH 3.3). According to the previous reasoning, even though the presence of *tert*-butanol inhibits the oxidation of oxalic acid via HO$^\bullet$ radicals in solution, this compound is believed to be oxidized on the surface of the activate carbon through a catalytic ozonation mechanism [20]. Though it was not possible to identify all the intermediaries of the reaction, the qualitative analysis of the HPLC chromatograms shows that, in the presence of *tert*-butanol, there is a higher amount of reaction products comparatively to the experiments in the absence of *tert*-butanol. Nevertheless, whenever activated carbon is present, a decrease in the concentration of those products is observed, which means that other mechanism, besides oxidation via HO$^\bullet$ in solution also occurs.

In the presence of *tert*-butanol the concentration levels of both oxalic and oxamic acids are generally lower than those detected without *tert*-butanol. In fact, the presence of *tert*-butanol does not inhibit the oxidation of SA but stongly inhibits further mineralization of the oxidation intermediates. Considering that both oxalic and oxamic acid are final oxidation products, it is possible that their concentrations are lower, as other by-products are also present when the reaction is carried out in the presence of a radical scavenger.

### 3.3. Considerations about the reaction mechanism

The removal of both BSA and SA, as well as the respective oxidation by-products, via ozonation in the presence of activated carbon is a result of a complex combination of homogeneous and heterogeneous reactions. Both direct and indirect ozone reactions occur in the liquid phase. Additionally, reactions between adsorbed species and oxygen radicals formed on the surface of the activated carbon are assumed to occur.

Regarding the non-catalytic decomposition of ozone in aqueous solution, it is established that it is initiated by the presence of HO$^-$ ions; so pH plays a major role in this process:

$$O_3 \xrightarrow{HO^-} HO^\bullet \tag{1}$$

Several authors have reported that activated carbon accelerates the decomposition of ozone [12–16]. It is consensual that both textural and surface chemical properties influence that decomposition, but doubts on the mechanism still remain. According to the literature, two possible pathways can explain the decomposition of $O_3$ in the presence of activated carbon. The first one assumes that activated carbon acts as an initiator of the decomposition of ozone, eventually through the formation of $H_2O_2$ [10], yielding free radical species, such as HO$^\bullet$, in solution [15]:
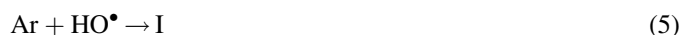
$$O_3 \xrightarrow{AC} HO^\bullet \tag{2}$$

Another possibility is the adsorption and reaction of ozone molecules on the surface of the activated carbon, yielding surface free radicals [12]:

$$AC + O_3 \rightarrow AC\text{–}O \tag{3}$$

where AC–O stands for any oxygen-containing active species on the surface of the activated carbon, which can react with adsorbed organic species [27].

Aromatic compounds (Ar) that are substituted by electron donor groups, such as –OH and –NH$_2$, have a high electronic density in *ortho*- and *para*- positions. Consequently, such aromatic compounds react actively in those positions with ozone by electrophilic attack. This results in the formation of several intermediates that are further transformed into saturated compounds (I), which cannot be mineralized by direct ozone attack. Additionally, HO$^\bullet$ radicals can also contribute to the oxidation of the aromatic compounds, as was shown for BSA, which seem to be refractory to direct ozone attack. The mineralization of the oxidation intermediates into $CO_2$ and inorganic ions (e.g. $NO_3^-$, $NH_4^+$, $SO_4^{2-}$), represented by P, occurs both in the liquid phase through HO$^\bullet$ radical attack, or on the surface of the activated carbon. Steps (4)–(8) schematically represent the proposed pathways.

$$Ar + O_3 \rightarrow I \tag{4}$$

$$Ar + HO^\bullet \rightarrow I \tag{5}$$

$$I + HO^\bullet \rightarrow P \tag{6}$$

$$AC + I \rightarrow AC\text{–}I \tag{7}$$

$$AC\text{–}I + AC\text{–}O \rightarrow P \tag{8}$$

Even though there is no experimental evidence, it is necessary to consider that adsorbed reactants might also react with dissolved ozone, or hydroxyl radicals from the aqueous phase, according to Beltrán et al. [28] that made similar assumptions regarding the ozonation of pyruvic acid catalyzed by activated carbon.

$$AC + Ar \rightarrow AC\text{–}Ar \tag{9}$$

$$AC\text{–}Ar + O_3 \ \text{ or } \ HO^\bullet \rightarrow I \tag{10}$$

It was shown that the presence of the radical scavenger (*tert*-butanol) induced different results depending on the aromatic compound studied. It inhibited the conversion of BSA, but no significant effect was observed for SA. However, in both cases the removal of oxidation by-products was influenced by the radical scavenger, which suggests the formation and reaction of HO$^\bullet$ radicals. This supplies experimental evidence for the occurrence of steps (5) and (6).

## 4. Conclusions

In the present work, the mineralization of two selected model compounds of sulfonated aromatic by-products found in industrial effluents was studied. The ozonation of benzene-sulfonic acid and sulfanilic acid leads to complete conversion of

both compounds after a short reaction period. As a result, the removal of these non-biodegradable compounds from aqueous solutions can be accomplished by chemical oxidation.

The presence of activated carbon during ozonation of BSA and SA increases their rate of degradation and mostly enhances the reduction of TOC. The use of a basic activated carbon is advantageous for this process. On one hand, adsorption of organic compounds is favoured and, additionally, basic activated carbons are believed to have an enhanced ability to catalyse the decomposition of ozone in aqueous phase into more reactive radical species, both on the liquid phase and on activated carbon surface.

Even though BSA seems to be more refractory to oxidation than SA, higher TOC removals are attained with solutions of the former compound. This is related with the characteristics of the intermediates formed, which seem to be more refractory in the case o sulfanilic acid. In fact, one of the final ozonation products is oxamic acid, which is a highly refractory carboxylic acid.

The presence of a radical scavenger during single ozonation evidenced the participation of HO$^\bullet$ radicals in the oxidation mechanism, especially in the degradation of BSA and in the mineralization of the oxidation by-products. In the combined treatment, the effects of radical scavengers were reduced due to the presence of activated carbon, which suggests that carbon surface plays a role in the reaction mechanism. Thus, activated carbon provides a surface where reactions between organic species and ozone or free radicals occur, i.e., acts directly as a catalyst.

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